

Synthesis of Vertical ZnO Nanorods on Glass Substrates by Simple Chemical Method

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Abstract. ZnO nanorods (NRs) have been synthesized by a chemical bath deposition (CBD) method on simple glass substrate that had been precoated by successive ionic layer absorption and reaction (SILAR) with a thin ZnO film. ZnO NR array was obtained by using zinc acetate and hexamethylenetetramine as aqueous solutions at optimized pH concentration and deposition time. X-ray diffraction (XRD) and SEM analysis were used to confirm the growth of ZnO nanorods. The pH and deposition time of the solution was found to influence the growth behavior of ZnO NRs. PL analysis also reflected the growth behavior of ZnO NRs.

1. Introduction

Semiconductor nanostructures have stimulated intensive interest to their tremendous technological applications which is due to excellent chemical and thermal stability. As an important wide band-gap semiconductor with a band-gap of 3.37 eV and large excitation binding energy of 60 meV at room temperature, Zinc oxide possesses a unique position among the materials owing to its superior and diverse properties such as piezoelectricity, chemical stability, and biocompatibility. In particular, ZnO nanoparticles are believed to be non toxic, biosafe, and possibly biocompatible and finds wide applications in day-to-day commodities like sunscreen lotion, cream, cosmetic and medicated creams, etc. Now a day's ZnO nanostructured films such as nanorods[1], nanowire[2], nanotube[3], nanodisks[4], nanocrystal[5], nanosheet[6] and so on has a wide range of technological applications including sensors [7], field emitters [8], optoelectronics [9], dye-sensitized solar cells [10] and in biological application [11]. In the recent years, numerous experimental techniques such as pulsed laser deposition[12], thermal evaporation[13], vapor transport deposition[14], filtered vacuum arc deposition (FVAD)[15], metalorganic chemical vapor deposition [16], metal organic vapor phase epitaxy [17], electrospinning [18], sputtering [19] etc. have been used to grow different ZnO nanostructures. However, the process is very complex and hard to be reproduced. On the other hand, in the past few years, it has been demonstrated that chemical process shows potential for the fabrication of ZnO nanorods due to its simply, low-cost and low-temperature process.

Among them, the simplest and the most economical method is solution growth technique. Compared with other methods, the solution growth technique has many merits such as large-scale manufacture and low synthesis temperature. Therefore, the solution growth process has been used for both ZnO seed layer growth and nanorod growth. Therefore, invention of a simple method to grow ZnO NR structure is still a big challenge to chemists and material scientist.

In our present work, a simple approach was followed, to grow ZnO NRs onto glass substrates. First, the ZnO thin film seed layer was deposited using successive ionic layer adsorption

and reaction (SILAR) method and corresponding NR growth was carried out using chemical bath deposition method (CBD).

2. Experimental

2.1 Chemical preparation details

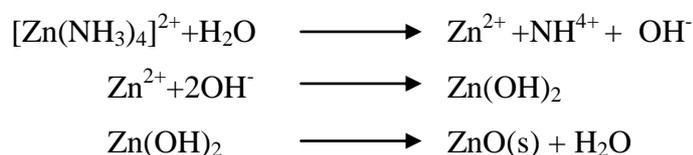
Glass and ITO substrates were used for the growth of ZnO seed layer by SILAR method. Prior to growth, the glass substrates were cleaned using a standard procedure. The procedure involved successive immersions of the substrates in chromic acid and double distilled water. The substrates were then ultrasonically agitated in detergent solution followed by rinsing in DD water and drying. Finally, they were subjected to vapor degreasing with isopropyl alcohol and dried. Finally the substrates were washed in ethanol with ultrasonic cleaner for 30 min. The cleaned glass substrates were then boiled in dilute sulfuric acid for 30 min and then completely rinsed in ethanol, acetone and de-ionized water. These procedures were adopted to get hydrophilic property in the substrates. Finally, the cleaned hydrophilic glass and commercial ITO substrates were used for the ZnO seed layer growth. To grow the seed layer, an aqueous solution of Zinc sulphate (ZnSO_4) complex with ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$) was prepared as cationic solution. The molar ratio of Zn: NH_3 is equal to 1:10. The anion solution was DD water. For the growth of ZnO NRs, an equimolar aqueous solution of Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) was prepared as zinc source and hexamethylenetetramine (HMT) with water was used as oxygen source.

2.2 Characterization details

The surface morphology of grown samples were analyzed using a scanning electron microscopy (SEM). The crystal structure details were obtained using x-ray ($\text{CuK}\alpha$ radiation) diffraction method. Jobin Yvon Fluorolog -3-11 model spectrofluorometer with xenon lamp as excitation source (450 W) was used for photoluminescence measurements. Raman spectra measurements were performed at room temperature with the Ar^+ laser as ($\lambda = 513.4$ nm) the excitation source to know the quality of grown ZnO NRs.

2.3 Formation of ZnO seed layer films by SILAR process

SILAR process involves the subsequent immersion of a given substrate in anionic and cationic solutions and rinsing procedures in between. In our case, a full deposition cycle for the growth of ZnO seed layer comprises of four steps. Fig. 1 (a, b) schematically illustrates the seed layer and NR growth processes. In the first step, the substrate is immersed in the beaker containing $\text{Zn}(\text{SO}_4)$ and ammonia solution, where Zn^{2+} with ammonia forms zinc ammonia complex. In this process, zinc ammonia is adsorbed onto the substrate. In the second step, the zinc ammonia adsorbed substrate is immersed into the beaker containing deionized water where the adsorbed zinc ammonia is converted into zinc hydroxide. In the third step, the substrate is immersed into the beaker containing deionized water and subjected to ultrasonic agitation thereby, the loosely bonded zinc hydroxide molecules are removed. In the final step, the substrate is immersed into the beaker containing deionized water kept at 80°C where the zinc hydroxide is converted to solid zinc oxide. Detailed experimental process were described in our pervious report [20]. The detailed chemical reactions involved in the SILAR growth process are given as follows:



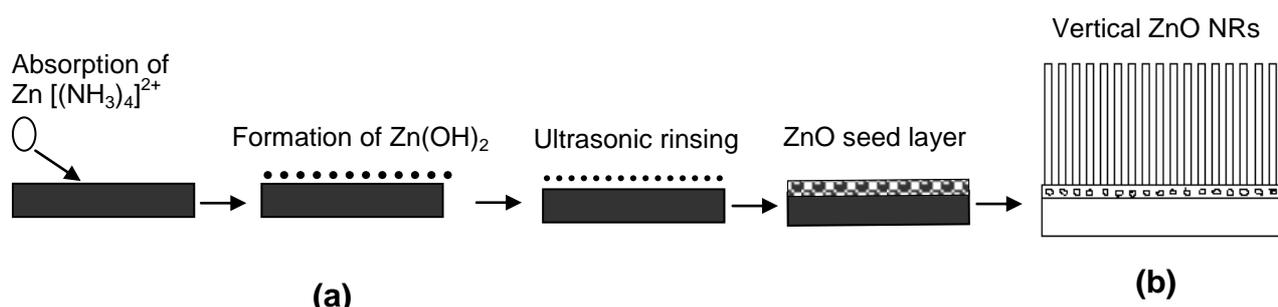
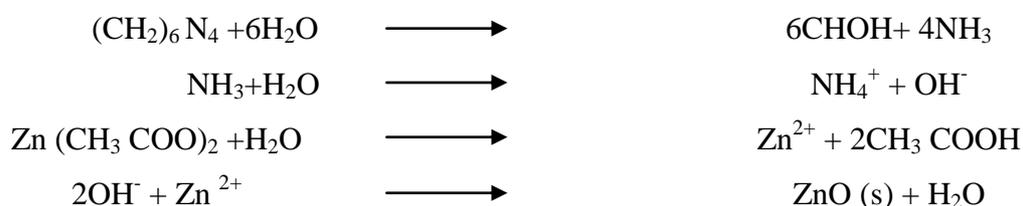


Figure 1. Schematic illustration of the (a) seed layer and (b) Nanorods growth processes.

2.4 ZnO NR growth process

The grown ZnO seed layer with different deposition cycles were used for the ZnO NR growth by keeping the same in a given chemical bath. The chemical bath was prepared by mixing equimolar aqueous solution of Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylene tetraammine (HMT) ($\text{C}_6\text{H}_{12}\text{N}_4$). To grow ZnO NRs, seed layered substrates were placed vertically inside the chemical bath at optimized pH of 6 and deposition time period of 8 hours. Finally, bath temperature was allowed to cool down to room temperature. The as-grown CBD films were carefully cleaned with double distilled water (DDW) and acetone for several times to remove residual salts and then dried at room temperature for further characterization.

The detailed chemical reactions involved in the growth of ZnO nanorods are as follows,



3. Results and Discussion

3.1 SEM analysis

Fig. 2 (a) is the SEM image of the ZnO seed layer grown onto a glass substrate. The SEM image shows a number of nano-sized particles randomly distributed on the surface of the substrate. Fig. 2 (b) shows the surface morphology of ZnO NRs grown on the seed layer by chemical method at optimized pH 6. The growth of ZnO by chemical method on seed layered glass substrate leads to a vertical growth with the diameter of the NRs ranging from 300 to 1 μm with perfect hexagonal shaped vertical NRs growth. Fig. 2 (c-d) corresponds to the Low and High magnified SEM image of the ZnO NRs grown at optimized deposition time of 8 hours. Here the diameter of the NRs ranges from 500 to 1 μm . In general, a difference is seen in the morphology between the two samples grown at two different growth parameter such as pH and deposition time. A similar growth process was carried out on ITO substrates at optimized condition. Fig 3 (a) Surface morphology of ZnO seed layer growth on ITO substrate shows random distribution of flower-like structure with voids in between. Each bunch of these structures is formed by small cluster of particles in size range of 500nm in diameter and particles in size around 50nm. Figure 3 (b) shows the corresponding ZnO

nanostructured growth on seeded ITO substrate. Surface morphology shows irregular shaped particles with no growth of vertical ZnO NRs. The main reason for this observation is due to the irregularity in the seed layer morphology.

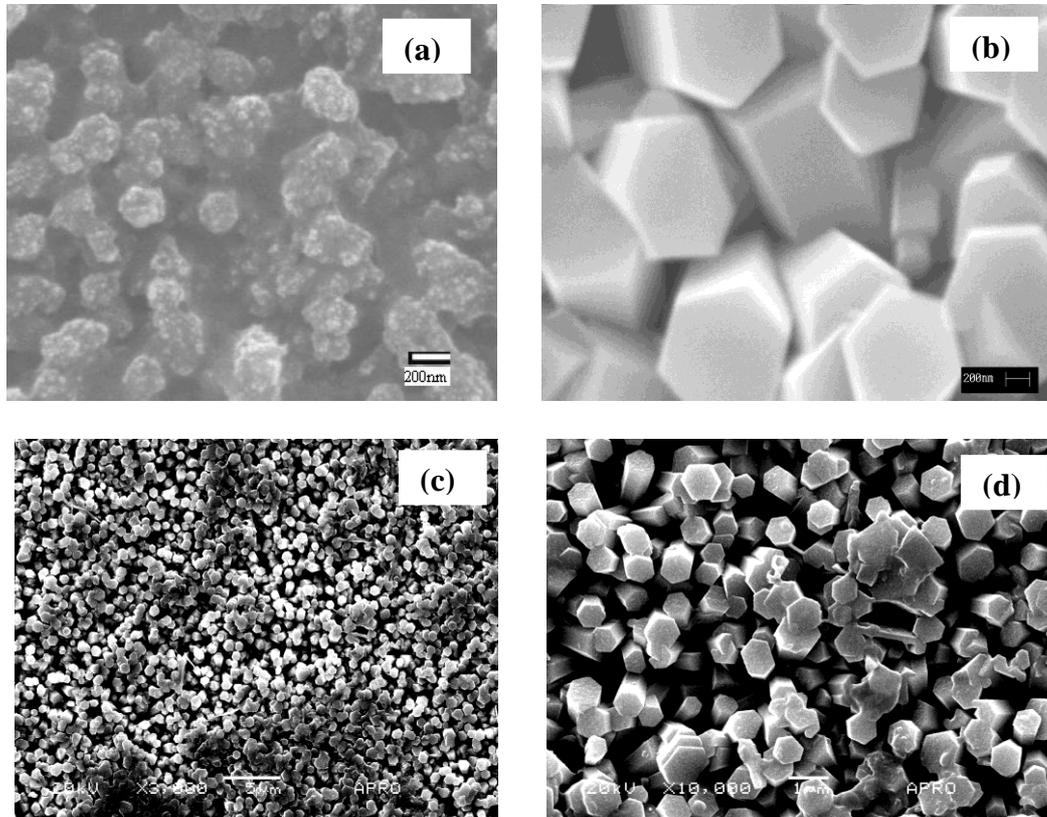


Figure 2 Aerial SEM image of (a) ZnO seed layer grown on glass substrates. (b) Vertical ZnO NRs grown on the seed layer at pH 6 grown at 200nm scale (c- d) Low and High magnified SEM image of NRs grown at optimized deposition time of 8 hrs

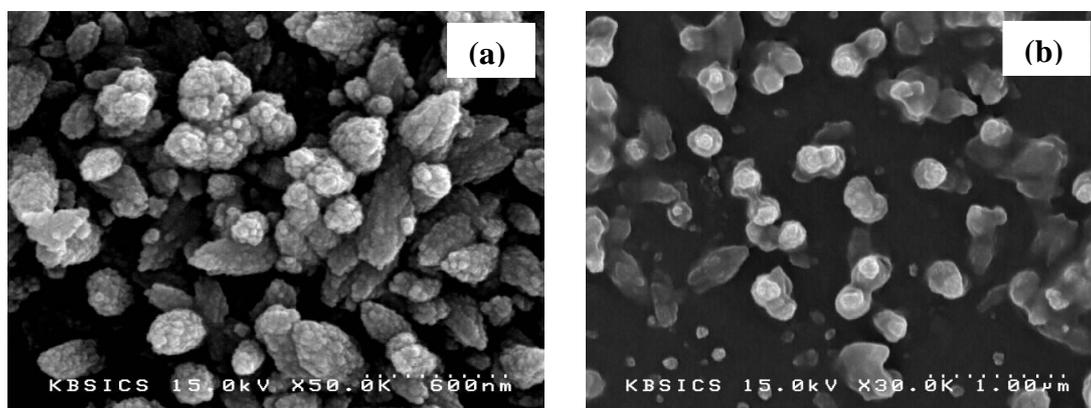


Figure 3. SEM image of (a) ZnO seed layer on ITO substrate (b) corresponding ZnO nanostructured grown on ITO substrates

3.2 XRD analysis

Fig. 4 (a) shows the XRD pattern of the ZnO seed layer grown on glass substrate. The XRD pattern shows a strong diffraction peak at 2θ value of 34.5° along (002) direction indicating the orientation of seed crystal along the c-axis. The XRD pattern of the as-grown ZnO NR on glass substrate at pH 6 and optimized deposition time of 8 hours has exhibits high (002) orientation indicating the preferential orientation of NR in the same direction as that of the seed crystal as shown in fig 4 (b-c). All the films show an additional peaks around 31.84° , 36.32° , 47.76° , 56.23° , 62.79° are indexed to (100), (101), (102), (110), (103) orientation of ZnO materials. In respect to ZnO peaks, no other residual peaks were observed.

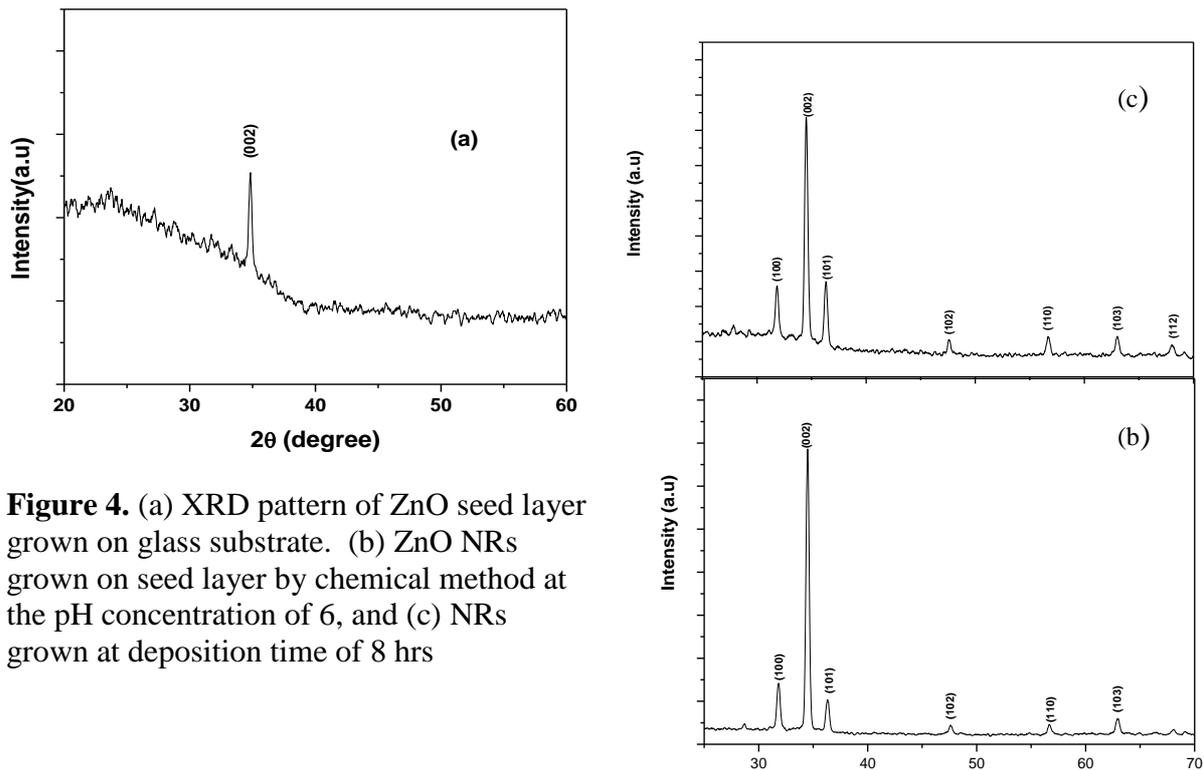


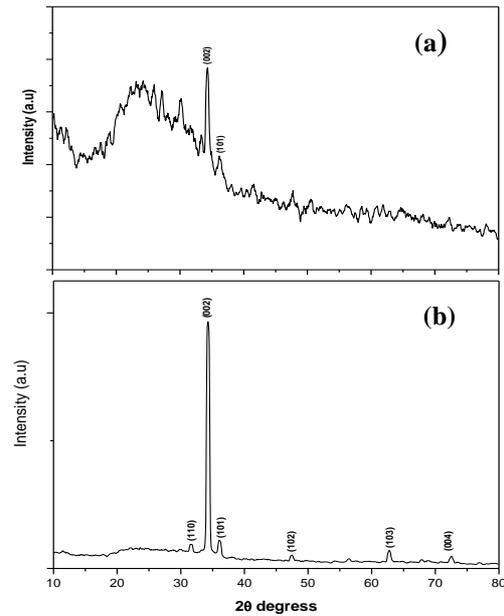
Figure 4. (a) XRD pattern of ZnO seed layer grown on glass substrate. (b) ZnO NRs grown on seed layer by chemical method at the pH concentration of 6, and (c) NRs grown at deposition time of 8 hrs

Fig. 5 XRD pattern of (a) ZnO seed layer growth (b) corresponding ZnO nanostructure growth on ITO substrate by CBD method. Fig 5 (a) shows the seed layer XRD spectra reveals a strong diffraction peak at 2θ value of 34.5° along (002) direction indicating the orientation of the seed crystal along the c-axis similar to glass substrate. From the XRD pattern, the crystallite size was calculated for (002) orientation ZnO films deposited on ITO substrates using Scherrers' formula:

$$D = 0.94\lambda/\beta \cos\theta$$

where D is the crystallite size, λ is the wavelength, β is the full-width at half-maximum (FWHM) and θ is the diffraction angle, and the average grain size of the ZnO seed layered film deposited on ITO, substrates was found to be approximately 16.2nm respectively. The corresponding ZnO nanostructured films on ITO substrate shows a major diffraction peaks at 2θ equal to 34.64° , which is corresponding to (0 0 2) orientation of wurtzite hexagonal structure of ZnO (JCPDS no. 36-1451). In addition to the (0 0 2) peak, we also observed other peaks such as (100), (101), (102), (103) and (004) which are corresponding to the hexagonal ZnO phase.

Figure 5. XRD pattern of (a) ZnO seed layer growth (b) corresponding ZnO nanostructure growth on ITO substrate by CBD method

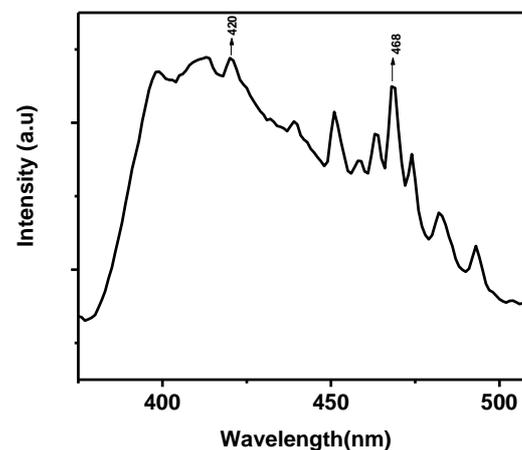


3.3 Photoluminescence (PL) analysis

The study of the luminescent properties of these ZnO nanostructures can shed some light on defects in the ZnO crystals and their potential as photonic materials. Fig 6 shows the PL spectra of ZnO NRs grown on glass substrate at optimized pH (6) values. In general, an edge emission at 385 nm and a broad visible emission around 400 to 530 nm are observed in ZnO related nanostructures [21]. The origin of edge emission is due to the recombination of electrons from conduction band to valence band. However, this emission is mostly degraded by the surface defect states resulted from the large surface to volume ratio of nanostructures and as well as by other imperfections at the boundaries which usually resulted from the growth methods and conditions.

B

Figure 6. PL spectra of ZnO NRs grown on glass substrate at optimized pH (6) values



The room temperature photoluminescence (PL) spectrum recorded from the seeded and ZnO and corresponding ZnO nanostructured film grown on ITO substrates by CBD method is shown in Figure 8(a, b). Normally ZnO nanostructures can exhibit a UV emission and visible emission (defect emission) while the green emission around is most common [22]. In our case, a sharp and strong UV peak at 385nm dominates the PL spectrum, and a weak and broad-green band is found in the range of 420–500 nm. The UV band emission of the array of ZnO nanostructures can be assigned to the emission from a free exciton under low excitation intensity, and the weak peaks in

the green band possibly originate from the electron transition from the level of the ionized oxygen vacancies to the valence band.

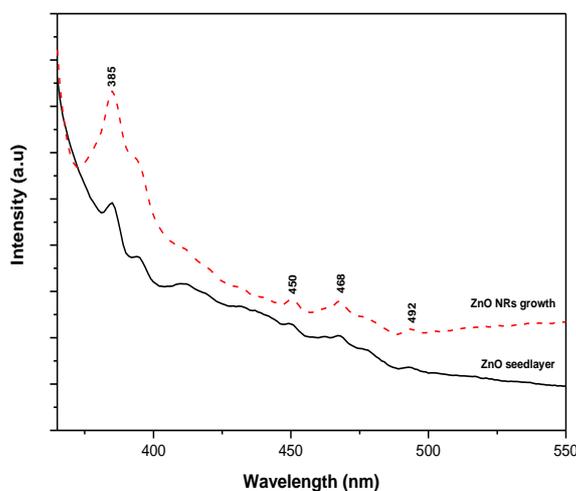


Figure 8. PL spectra of ZnO seed layer and corresponding nanostructured growth on ITO substrate at an excitation wavelength of 360 nm.

4. Summary and Conclusions

In summary, we demonstrated a new and simple approach to grow vertical ZnO NRs. First the ZnO seed layer was grown using successive ionic layer adsorption and reaction (SILAR) method and secondly, vertical ZnO nanorods growth was carried using chemical bath deposition method (CBD). The XRD spectra from the seed layer surface has shown preferential (002) orientation which was well suited for 1D Nanorod growth. From the SEM analysis confirmed the vertical ZnO Nanorods grown on glass substrates. The SEM and XRD analysis shows influence of the nature of seed layer on the growth of NRs. Though, this simple and cost effective method needs a further improvement in the optimization of growth conditions, we hope that the present approach can be a potential method to grow vertical NRs.

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